PATENT SPECIFICATION

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C1A 13

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(54) IMPROVEMENTS IN OR RELATING TO A METHOD FOR THE REDUCTION OF HAZE IN BEER

(71) We, UNILEVER LIMITED, a company registered under the laws of Great Britain, of Port Sunlight, Birkenhead, Cheshire, England, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the treatment of beer and more particularly to a process for improving beer by reducing its tendency to form haze on storage.

The term "beer" in this specification is to be construed in the broad sense to include beverages such as ales, lagers and stouts and other liquids which present haze problems on storage.

Various processes have been proposed hitherto for clarifying beer by the removal of the various haze forming constituents. The haze or turbidity present in beer can sometimes be removed by filtration techniques but in some beers, on standing, a further haze or turbidity develops and, if the beer has by this time been bottled or canned, removal is generally not practicable. It is therefore desirable to remove both the haze developed during production or on standing prior to final processing and also haze forming materials which may develop haze during the time the beer is standing after the final processing but before being consumed. It is desirable that the materials used for treating the beer do not remove from the beer components which are essential to the character of the beer such as flavour forming components, head-forming components and colourings.

Various materials such as bentonites, active carbon, nylon, polyvinyl pyrrolidone and certain silicas have previously been proposed for this purpose and are to a greater or lesser extent effective. However, the cost of such treatment arising both from the materials used and from processing costs such as filtration and storage are not insignificant and any reduction, particularly when under some circumstances this can be accompanied by increased efficiency, and without a reduction in desirable characteristics such as flavour and head-retention, is attractive. In addition, some food purity laws require that no soluble materials be added to beverages.

It has now been found that certain high surface area silica xerogels, having a fairly closely defined mean pore diameter (MPD), give good results in respect of haze removal and, have no ill-effects on head retention and, in some cases, even improve this particular characteristic of the beer.

Accordingly, the present invention provides a process for the treatment of beer which comprises treating the beer with a silica xerogel having a surface area of between 700 and 1200 m^2/g, a pore volume at least 0.7 ccs./g. and a mean pore diameter from 25 to 80 Å and separating the silica from the beer.

One accepted indication of the haze reducing or stabilising efficiency of slicas used in the treatment of beers is the "saturated ammonium sulphate precipitation limit" test. In this test saturated ammonium sulphate solution is added to samples of treated and untreated beer and the quantity of solution required to cause a sudden increase in turbidity as measured by a reflectometer, is measured. The difference in quantity required by the treated and untreated beer, often expressed as Δ ml SASPL, is an indication of the haze reducing efficiency of the silica under test.

The head retention values (HRV) referred to in the present specification were determined by the following test.

Samples of beer were treated at 0°C with a sample of silica (1 g. as SiO_2 per litre) and left standing for 5 minutes or 24 hours. Then the silica was filtered off. The treated beer was carefully run into a tube to a height of 10 cm., the tube having at its lower end a sintered glass disc through which carbon di-

SEE ERRATA SLIP ATTACHED

oxide gas can be bubbled into the beer to form a head of foam. Bubbling is continued to a pre-determined height (32.5 cm.) and then the gas supply is reduced to just support the beer on the disc whereupon the foam starts to collapse. The head retention value is 1.44 multiplied by the time in seconds taken for the boundary between the level of the liquid beer and the bottom surface of the foam to pass between marks at 5 and 7.5 cm. on the tube.

Whilst we do not wish in any way to be bound by the following theories these theories do offer a possible explanation of the way in which the process of the present invention works.

It appears to be possible that the stability of foam on beer ("head") is dependent on a positive or boosted and negative or suppressing head factor and that these two factors are constituted by materials of significantly different particle size or shape hence by selecting silica xerogel having a closely defined MPD the negative factor can perhaps be preferentially or selectively removed.

Accordingly in a preferred embodiment of this invention the mean pore diameter of the silica xerogel is from 40 to 80 Å.

It will be understood that the MPD is an average figure and can be the result of a wide or narrow actual distribution of pore widths and the preferred silicas for use in this invention have a wide distribution of pore widths and not a relatively narrow one as has been the case with hitherto proposed high pore volume xerogels.

For efficient operation of the process of this invention and particularly to produce the best results in respect of contact time of beer and silica and ease of separation of beer from the silica it is desirable that a significant proportion of the silica is present as fine particles. The average particle size of the silica is preferably less than 20 microns.

As with the MPD discussed above, the actual particles on which the average figure is based can be made up in various ways and for the process of this invention it is desirable that at least 10% by weight of the silica is made up of particles smaller than 10 microns. Whilst it will be appreciated that the accurate assessment of particle size is difficult when the particles are less than about 3 microns it has been found that for good Δ ml SASPL figures a significant number of particles less than 5 microns is desirable.

Accordingly silica xerogels having at least 10% by weight of their particles less than 5 microns are particularly useful.

The quantity of silica used in the treatment of beer will be to an extent dependent on the actual xerogel selected and on the quality and age of the beer to be treated.

In general using the above defined silica xerogel it will not normally be necessary to use more than 1 g. of silica per litre of beer to be treated.

Xerogels useful in the present invention may be made by various processes.

A preferred process is a continuous process in which the silica is produced by mixing an acid and sodium silicate under conditions of high shear.

In this process the silica is prepared by reacting together under high shear an alkali metal silicate and an acid solution. The silica produced can readily be acid washed to yield a hydrogel of greater surface area and pore volume than the original silica, and this hydrogel on drying and comminuting provides a xerogel having the characteristics which make it useful in the process of the present invention.

Samples 1—5 set out below in Table I were prepared by the preferred process in which the acid and silicate are reacted together under high shear.

TABLE I

Samples	1	2	3	4	4a	4b	5
Sodium silicate (Na_2O:SiO_2 1:3.3) SiO_2 content %	25.2	25.2	25.2	25.2	25.2		25.2
Sulphuric acid normality	10.8	10.8	11.4	11.4	11.4		11.4
pH at gelation	1.5	3.0	8.5	6.5	6.5		8.5
Weight of hydrogel kg.	90.8	90.8	90.8	90.8	90.8		100 gm.
Washing technique	Hydrogel aged for 30 mins at 60°C. in 454 litres water 1. washed sulphate free with town water 2. washed with 454 l 3% w/v ammonium sulphate 3. sulphate free town water	Hydrogel washed for 30 mins with 227 litres 1N sulphuric acid at 20°C. washed sulphate free with town water	as for 2 but using 0.1 N sulphuric acid	as for 3	as for 3		Hydrogel washed with 0.2N sulphuric acid 400 g at 25° for 25 mins then washed with deionised water to remove sulphate
Drying	spray-dried 175 — 200°C	as 1	as 1	as 1	as 1	rotary drier	oven dried 200°C.
Milling	Hammer Mill	air micronised	as 2	as 1	as 2	as 1	air micronised as hydrogel 3 before acid washing.

Samples 6—8 were prepared by a batch process in a beaker using a high shear mixer. The details are set out in Table II below.

TABLE II

Samples	6	7	8
Sulphuric acid normality	9.3	9.3	3.6
Vol (cc)	40	50	50
Sodium silicate % SiO_2	21.4	21.4	9.9
Vol (cc) silicate solution	160	200	200
Gelation pH	8.0	7.8	8.5
Hydrogel wt. g.	100	100	100
Ageing time (mins)	45	120	120
Sulphuric acid treatment			
Normality	0.2	0.2	0.2
Vol (cc)	400	400	400
Temp (°C)	20	20	20
Contact time (mins)	30	30	30

The sodium silicate was added to sulphuric acid and powerfully agitated with a "Silverson" mixer. (The word "Silverson" is a Trade Mark.) After the hydrogel had been treated with acid, the bulk of the sulphate was removed by washing with deionised water (ambient temperature) followed by oven-drying at 200°C.

Samples of various silicas defined in Tables I and II were taken and evaluated in respect of their stabilising efficiency on a pale ale normally sold as a bottled beer. 1 g of SiO_2/litre of beer was used and the results are set out in Table III below.

The silica can conveniently be added to the beer as an aqueous slurry and then separated after, for example, 5 minutes contact time, by filtration, if desired in the presence of a filter aid. Alternatively, the silica may be stirred into the beer and the beer removed after the silica has settled.

TABLE III

Sample of Silica	SA m^2/g	PV ccs/g	M.P.D. Å	A.P.S. μ	Δ ml. SASPL.
1	837	0.89	43	13.7	1.9
2	930	0.70	31	2—5	2.2
3	715	1.10	62	2.4	2.4
4	795	1.01	51	14	2.1
4a	769	0.97	50	2.2	2.5
4b	775	0.94	49	12.2	1.8
5	794	1.17	59	17.9	2.1
6	943	0.89	38	25.9	1.7
7	819	0.93	45	24.7	1.7
8	890	0.71	32	24.2	1.8

M.P.D. — mean pore diameter.

A.P.S. — average particle size.

S.A.S.P.L. ml of control beer — 1.2

PV ccs/g — Pore Volume cubic centimetres per gm.

SA m^2/g — Surface area sq. metres per gm.

Further quantities of samples 4 and 4a were used in pilot plant brewery trials. The quantities used were 12 oz/barrel (2g/l) and the beer was a pale ale. The results are set out in Table IV below.

TABLE IV

	Control	Sample 4	Sample 4a
S.A.S.P.L. ml	0.9	3.0	3.2
Δ ml SASPL	0	2.1	2.3
Head retention	132	127	127
Bitterness	19.0	20.2	18.8
Total N_2 ppm	371	330	340
Lundin A Fraction average	100	53	62

The results in Table IV indicate that the use of xerogels according to the present invention even at the relatively high dosage rate of 2g/l has no significant effect on flavour in terms of bitterness. This is determined as the isohumulone content.

The drop in Lundin A fraction content is a further indication of the useful haze removing properties of these silicas.

Lundin (J. Int. Brewing 1931 Vol. 37) has devised a method of nitrogen fractionation that separates proteins according to their molecular weight. The Lundin Fraction A is the protein precipitated by tannin and represents the high molecular weight nitrogen compounds which are responsible for haze formation. A reduction in the fraction indicates a reduction in the haze forming protein.

No major change in head retention characteristics indicates no problems arise in this connection.

To demonstrate the improved stabilising properties of the products of this invention when compared to prior art xerogels, Sample 4 and a commercially available xerogel (Xerogel C) were taken and evaluated in respect of the stabilising efficiency of two pale ales. Two dosage rates of 0.5 and 0.75 g/litre of beer were used and the results are set out in Table V below. The results in Table V show that although the Xerogel C treatment gave a similar reduction in haze to Sample 4 as shown by the SASPL test there was a larger drop in the HRV. The HRV of the beer treated with Sample 4 was not statistically different from the control.

TABLE V

					Beer 1			Beer 2		
	SA (m^2/g)	PV (cc/g)	MPD (Å)	ASP (μ)	Dosage g SiO_2/l	SASPL (ml/10 ml of beer)	*HRV (Σ sec)	Dosage g SiO_2/l	SASPL (ml/10 ml of beer)	*HRV (Σ sec)
Control	—	—	—	—	—	0.7	137	—	1.5	151
Sample 4	795	1.01	51	14	0.75	2.4	135	0.50	3.2	149
Xerogel "C"	360	0.92	103	12	0.75	2.3	133	0.50	3.3	146

* A difference $\geqslant 3\ \Sigma$ sec between the control beer HRV value and the treated beer HRV value is significant at 95% confidence level.

WHAT WE CLAIM IS:—

1. A process for the treatment of beer which comprises treating the beer with a silica xerogel having a surface area of between 700 m^2/g and 1200 m^2/g, a pore volume at least 0.7 ccs/gm and a mean pore diameter from 25 to 80 Å and separating the silica from the beer.

2. A process as claimed in Claim 1, in which the average particle size of the silica is less than 20 microns.

3. A process as claimed in Claim 1 or Claim 2, in which at least 10% by weight of the xerogel is made up of particles smaller than 10 microns.

4. A process as claimed in Claim 3, in which at least 10% by weight of the xerogel is made up of particles smaller than 5 microns.

5. A process as claimed in any one of the preceding claims, in which the distribution of pore sizes on which the mean pore diameter is based is a wide one.

6. A process for the treatment of beer, as claimed in Claim 1 in which the silica is a xerogel as defined in Table III or Table V.

7. Beer treated by a process as claimed in any one of the preceding claims.

J. E. FARNDON,
Chartered Patent Agent.

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SPECIFICATION No. 1,279,250

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Page 6, TABLE V, Heading 5th Column, *for* ASP *read* APS
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THE PATENT OFFICE
31st July 1972

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